FINAL REPORT

PHYSICAL PROPERTIES OF LEAD SELENIDE FILMS

FOR - Department of the Navy
Bureau of Naval Weapons
Missile Guidance and Airframe Division
Washington 25, D. C.

23 May 1963

Contract NO_W 62-0925-c
Section A, Item 3

SBRC
SANTA BARBARA RESEARCH CENTER
A Subsidiary of HUGHES Aircraft Company

SANTA BARBARA RESEARCH CENTER

A Subsidiary of Hughes Aircraft Company

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SBRC

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SBRC

INTRODUCTION

Under two contracts during the last twenty-two months, SBRC has received support from the Naval Bureau of Weapons to perform research and development in processes and techniques leading to more producible and more stable lead selenide detectors.

The first program, under contract NOw-61-0403-c, was conducted over a 12-month period. Considerable effort was expended in performing high temperature storage tests on new packaging techniques for refrigerated PbSe detectors. Two new techniques have been established that greatly improve PbSe detector stability. Through the joint efforts of this program, a company-sponsored program, and an Air Force hardware program, a "fix" on the lead selenide film stability problem was made. Consequently, many operational infrared systems are presently using SBRC PbSe detectors as the heart of their equipment. Although a successful "fix" had been established, further research and development work was considered necessary for better understanding of the mechanism of photoconductivity within these films. Thus, a greater awareness of the reasons for the environmental instabilities could be obtained.

During the latter part of this program, the SBRC Physics Department directed its effort toward a greater comprehension of the physical nature of these chemically deposited films. This effort was extended for an additional eight months under contract NOw 62-0925-c. The contract was later extended for two more months and work was completed on 27 April 1963. The details of the first 6-month effort have been previously reported in two quarterly reports and will not be repeated here. However, the significant results of the first six months will be summarized in this final report. This report will stress the information that has been gained concerning PbSe films during the last four months of this contract.

SBRC

SUMMARY OF FIRST SIX MONTHS EFFORT

The first two quarterly reports of this program described the details of several experiments that were performed to obtain new information about the characteristics of PbSe films.

The results of these studies can be summarized thus:

1) The performance of standard PbSe detectors as a function of temperature was analyzed experimentally. This study proved that the optimum bias of a liquid nitrogen cooled detector occurs when the Joule heating caused by the bias power is sufficient to heat the film to a temperature significantly above 77°K. The exact optimum temperature depends to a degree on the sensitization of the film.

2) AC-Hall effect equipment has been used as a tool to separate the effective carrier concentration from the effective carrier mobility within the film. It has been possible to examine the temperature dependence of the Hall coefficient and effective Hall mobility as a function of infrared background radiation and visible background radiation. These measurements provide valuable information on the primary photoconductivity of the film as well as the secondary photoconductivity within the film ("flash effect").

3) These AC-Hall effect measurements have also provided a method for studying the electrical stability of PbSe films when exposed to different surface environments. For example, 35 days of continuous high-vacuum pumping caused an order of magnitude decrease in carrier concentration in a fairly stable sample. Presumably, this change is caused by a loss of surface adsorbed water. Some films show an order of magnitude change in carrier concentration in less than one day of high vacuum exposure. Exposure to high humidity restores the original carrier concentration.

4) Experiments were conducted in cooperation with the Nuclear Effects Department of Hughes-Fullerton to examine the effect of adverse nuclear environments on the electrical performance of PbSe detectors. The results of these experiments indicated that, during short duration gamma radiation bursts of several microseconds from the Hac Linac, the PbSe detector is "blind".

However, the normal detectivity is recovered within the characteristic detector time constant. A comparatively small resistance decrease was observed after each Linac burst. This effect is similar to the long period "flash effect" observed when cooled PbSe is exposed to intense visible or ultraviolet radiation. This flash effect would not cause any serious difficulty as long as the integrated exposure to the gamma flux is small.

SUMMARY OF RECENT RESULTS

Photo-Hall Measurements on PbSe Films

The most significant experiments performed during the period between 1 January and 27 April 1963 were comparisons of the electrical characteristics of a sample film from a representative "stable" deposition with those of a sample film from a representative "unstable" deposition. For many years bitter experience has found that some sensitized films are far more susceptible than other films to environmental changes. In other words, while some films can withstand transfer from laboratory air to high vacuum storage without a severe increase in resistance, other films can exhibit resistance increases of one to two orders of magnitude.

Deposition #24-1 was selected for these experiments as representative of an unstable film. Deposition #4002-134 was selected as a representative stable layer. The first measurements were performed on a Hall sample made from deposition 24-1. The initial film resistance of this Hall sample was 3.5 megohms/square at 77°K. AC-Hall measurements were performed on this sample while the sample was mounted in the standard Hall dewar and sealed to a dynamic all-glass vacuum system. During the course of these measurements, it was observed that the Hall coefficient drifted up severely. After pumping overnight, the sample resistance was observed as about 100 megohms (about 25 megohms/square). It was impossible to perform accurate Hall measurements on a sample with such a large impedance. The film was then exposed to the laboratory air (relative humidity $\sim$50%) to readsorb sufficient H_2O to bring the resistance back down; and the silicone coating described in Report QR3220-2 was applied to tie up the surface adsorption sites and effectively retard the change in resistance under high vacuum conditions. In this manner, the necessary measurements were performed on this representative sample of a film that was so unstable, accurate extended measurements were not possible.

Aided by a series of constant boiling cryogenic liquids, it was possible to measure the electrical conductivity (σ) and AC Hall coefficient (R_H) as a function of temperature with the film exposed to several different temperature backgrounds. The results of these measurements are reported in Fig. 1 for three different background temperatures, viz, 300°K, 400°K, and 500°K. These temperatures were achieved using a conducting glass plate as a resistance heater in front of the silicon window of the Hall dewar. Two parameters are shown in Fig. 1, (a) the Hall coefficient (R_H), which is interpreted as a measure of the reciprocal of the effective hole concentration $R_H=1/ne$, and (b) the effective Hall mobility (μ^*) of the holes, where $\mu^*=R_H\sigma$.

Figure 2 shows the results of similar measurements performed on a much more stable film (#4002-134-1). An additional background temperature of 145°K was included by immersing the lower part of the side-looking Hall dewar in Freon 14. A comparison of the results shown in Fig. 1 with those in Fig. 2 may be generalized in these observations:

1) The major photoconductive change in both stable and unstable films is the change in the effective carrier mobility.

2) The carrier concentration in the stable sample is about an order of magnitude larger than the carrier concentration in the unstable sample.

3) The carrier concentration in the unstable sample is dependent on the incident radiation.

4) Within the experimental error of about 10%, the carrier concentration in the stable sample is not dependent on the incident radiation for the magnitudes of radiation that were used.

5) The carrier mobility in both samples is approximately the same order of magnitude.

A quantitative comparison of these results was attempted using calculated effective photon intensities from 0 to 6.5 microns for the different source temperatures. A table of these results calling T_1 the higher temperature and T_o the lower temperature was prepared from the results shown in Figs. 1 and 2, at a 77°K sample temperature. Also included in this table are some carrier lifetime comparisons that will be discussed later.

TABLE I

Sample	T_1	T_o	Q_1/Q_o	n_1/n_o	μ^*_1/μ_o^*	τ_o/τ_1	Remarks
24-1	400	300	9.3	1.5	1.9	-	Unstable
	500	400	4.1	1.4	1.5	-	
4002-134-1	300	145	6200	1.0	1.2	-	Stable
	400	300	9.3	1.0	1.2	2.3	
	500	400	4.1	1.0	1.2	1.5	

The results in Table I show that the dc resistance of PbSe films does not depend linearly on the background radiation as it does for extrinsic germanium detectors in the background limited region. It is also apparent that carrier concentration, carrier mobility, and carrier lifetime are all dependent on background radiation at low temperature. There is no simple numbers mechanism that can explain this behavior. It is felt that the population of complex radiative recombination centers at or in the intergranular oxide barrier directly affects the mobility of carriers through the oxide regions between the grains.

The majority carrier lifetime and majority carrier mobility will both be strongly dependent on infrared background radiation. The effect of radiation on the density of majority carriers in this model will depend to a large degree on the residual density of holes in the valence band after sensitization (oxidation).

A large hole concentration will be less affected by infrared radiation, visible radiation, or surface changes than a smaller hole concentration.

Photoconductive Lifetime Measurements

The photoconductive lifetime of Hall sample #4002-134-1 was also determined as a function of temperature and background. For these measurements, a zirconium concentrated arc source was used in conjunction with a high-speed focal plane chopper to achieve square light pulses with an onset time of 0.3 microseconds. Mercury was introduced into the Hall dewar flask and a copper-constantan thermocouple was inserted in the mercury to monitor the mercury temperature. Comparatively low bias power levels were used to prevent Joule heating of the sample and the film temperature was believed to be nearly the same as the mercury temperature. The mercury was then frozen and cooled to liquid nitrogen temperature. Time constant measurements were made by photographing the square wave response on the oscillograph as the detector slowly warmed to room temperature. These measurements were repeated for three different levels of background radiation, viz:

Background Temperatures	Effective Photon Flux (photons/cm^2-sec)
300°K	7.60×10^{16}
400°K	7.05×10^{17}
500°K	2.85×10^{18}

The results of these measurements are shown in Fig. 3. This set of curves shows the manner in which the lifetime in the low temperature regions is changed by increasing the background radiation level above the normal room temperature ambient level. To achieve lifetime measurements over a wide range of background levels, one can reduce the normal 300°K radiation by the use of cutoff filters. Unfortunately, due to an accident with Hall sample #4002-134-1, it was necessary to substitute a "sister" sample for these measurements. Hall and conductivity measurements on sample #4002-134-2 were quite similar to #4002-134-1 over the temperature range from 77° to 300°K. See Fig. 4. After obtaining D* and lifetime measurements of this unshielded and unfiltered sample as a function of temperature, a cold quartz filter cutting off at about 4.8 microns was used for the next set of measurements. Finally, a 3.1-micron interference-type cutoff filter was combined with glass to cut off the film response beyond 3.1 microns. The calculated flux levels for a 300°K background under these situations are presented below, along with the measured time constants at low temperature.

TABLE II

Wavelength Region (microns)	Effective Photon Flux (photons/cm^2-sec)	Lifetime (microseconds)
0 to 6.5	7.6×10^{16}	24
0 to 4.8	9.6×10^{15}	92
0 to 3.1	5.8×10^{13}	400

The temperature dependence of the lifetime in this sample is shown for these background levels in Fig. 5. In the case of the 3-micron cutoff filter, it was necessary to extend the temperature measurements down to liquid hydrogen temperature.

The lifetime values in the low temperature (flat) region of Figs. 4 and 5 are plotted on log-log paper in Fig. 6. This graph extends over more than four orders of magnitude in background flux level. A straight line can be drawn through most of the points shown. The points outside the line are within the limits of experimental error. A determination of the slope indicates that for this particular deposition

$$\tau \propto Q^{-0.37}$$

This type of measurement should be conducted for other samples of different deposition to determine whether this empirical result is representative of all samples.

Unfortunately D* values were determined for only two of the five different radiation levels used. However, these two values have been included for Fig. 6. The slopes are very similar. For this particular sample, one can conclude that

$$D^* \propto \tau \propto Q^{-0.37}$$

Intermediate PbSe Films

To date, all of the work on this program has been concerned with measuring the electrical characteristics of PbSe films optimized for best performance at low temperatures for use with liquid nitrogen. However, in recent years, another type of PbSe film has been developed at SBRC. This type of film is optimized during sensitization for best performance near dry ice temperature. Although this detector is not as widely used as the cooled variety, it is felt that it will be used quite extensively in the future. This "dry ice" detector has a detectivity that is at least four times higher than InSb or any other known 3-to-5-micron detector operated in this temperature range. The chief advantage of intermediate PbSe is its greatly reduced cooling requirements. Consequently, alternate cooling techniques such as Peltier cooling or radiation cooling are possible. These techniques are not possible in the temperature region below about 145°K.

Both of these films are formed by the same chemical deposition technique. The difference occurs during the sensitization process. The intermediate temperature PbSe film is more highly oxidized than the low temperature PbSe film. The resistance of intermediate PbSe is considerably higher than low temperature PbSe. For this reason, practical intermediate PbSe detectors are frequently made using interlaced electrodes in order to reduce the resistance.

Using two representative samples of each type, measurements were made to characterize the performance of these two types of detectors. Since the detectivity of a detector is determined by its photoconductive lifetime, this parameter was monitored as a function of temperature for all four samples. The results are shown in Fig. 7. Samples 6070-17-18 and 6070-32-44 are intermediate temperature type elements from two different depositions. There is a distinct difference in their lifetime behavior at low temperatures, although they are not so far apart in their intended operating temperature range.

The low temperature elements JW1311-27 and JW1311-28 are both from the same deposition and they have similar characteristics. The comparison of results between the intermediate type and the low temperature type is the most striking. The intermediate lifetime curve is both increased and shifted to higher temperatures. The JW1311 detectors have a maximum lifetime at about 105°K, while the 6070 detectors have their maximum lifetime at about 177°K. The lifetime of the 6070 detectors is down to one-half of the maximum at about 232°K, while the lifetime of the JW1311 detectors is down to one-half of the maximum at 145°K.

Figure 7 also shows a tabulation of the D* values of these detectors at peak wavelength. The 6070 detectors were measured at dry ice temperature, while the JW1311 detectors were measured at liquid nitrogen temperature. All of the detectors reported here were operated with a full 2π-steradian field of view looking at a 300°K background.

CONCLUSIONS

1) A much better understanding of the photoconductive mechanism in PbSe films has been obtained during the course of this program.

2) Barrier modulation is the dominant photoconductive mechanism in cooled PbSe films.

3) The relative magnitude of the modulation of carrier concentration by infrared radiation depends on the carrier concentration within the particular film.

4) The magnitude of carrier concentration within the film at low temperatures is strongly surface dependent in unstable films. Adsorption of water vapor can increase the carrier concentration by one to two orders of magnitude. Desorption of water vapor can decrease the carrier concentration by a comparable amount.

5) Stable films are those having a large concentration of carriers approaching $10^{17}/cm^3$ at low temperature.

6) The process-variable difference between stable and unstable films is still unknown.

7) Two techniques are now available for improving the stability of PbSe films. One technique involves the use of a protective coating to tie up the surface-adsorption sites and reduce the effect of adsorption and desorption of water. The other technique involves the encapsulation of the film in a small amount of controlled-humidity air to establish a controlled equilibrium with the surface.

8) The detectivity of PbSe films is primarily dependent on the majority carrier lifetime.

9) With a 2π-steradian field of view and 300°K background, at temperatures above about 150°K, low temperature type PbSe films have a lifetime limited by the radiative recombination of thermally-generated electrons and holes directly between conduction band and valence band.

10) Below about 145°K, the lifetime is probably limited by the presence of recombination centers of the Shockley-Reed type in the region of the surface barriers.

11) The lifetime and detectivity increase as the background radiation decreases. For film #4002-134,

$$D^* \propto \gamma \propto Q^{-0.37}$$

12) Intermediate temperature type PbSe films can be operated at a temperature which is about 70°K higher than the low temperature variety.

13) Experience has shown that intermediate temperature PbSe films are more stable than the low temperature variety.

14) The electrical characteristics of the intermediate variety have not been thoroughly evaluated to date.

RECOMMENDATIONS FOR FUTURE WORK

The following recommendations can be made for future work with PbSe films:

1) Evaluate the characteristics of intermediate PbSe films to obtain a better understanding of the differences that exist between this type of film and the low temperature variety.

2) An evaluation of lifetime and detectivity of PbSe films as a function of background radiation and temperature for both varieties should be extended to determine the limits of improvements that can be achieved by radiation shielding. Past experience has indicated that some films show a much larger range of improvement than other films. The reason is not understood.

3) A study of the variability in thickness, grain size, composition, and uniformity of PbSe films should be undertaken to try to obtain a better correlation between "high detectivity" and "low detectivity" and "stable" and "unstable" films.

D.E. Bode, Project Manager

H.A. Graham, Project Engineer

R.M. Talley, Manager
Santa Barbara Laboratory

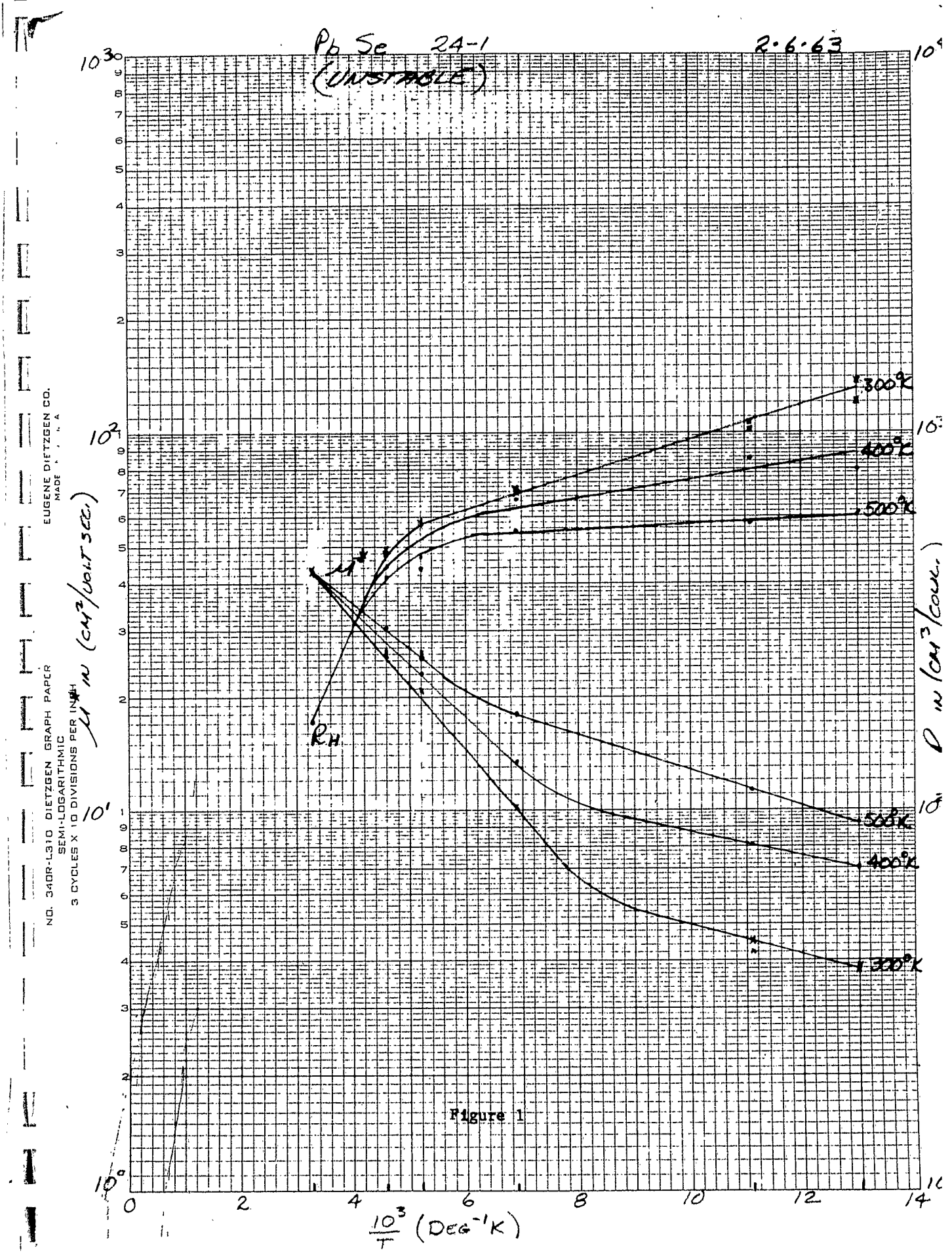

Pb Se 24-1
2·6·63
(UNSTABLE)
300°K
400°K
500°K
R_H
μ
μ_H in (cm²/volt sec.)
σ in (cm³/ohm.)
$\frac{10^3}{T}$ (Deg⁻¹K)
0
2
4
6
8
10
12
14

Figure 1

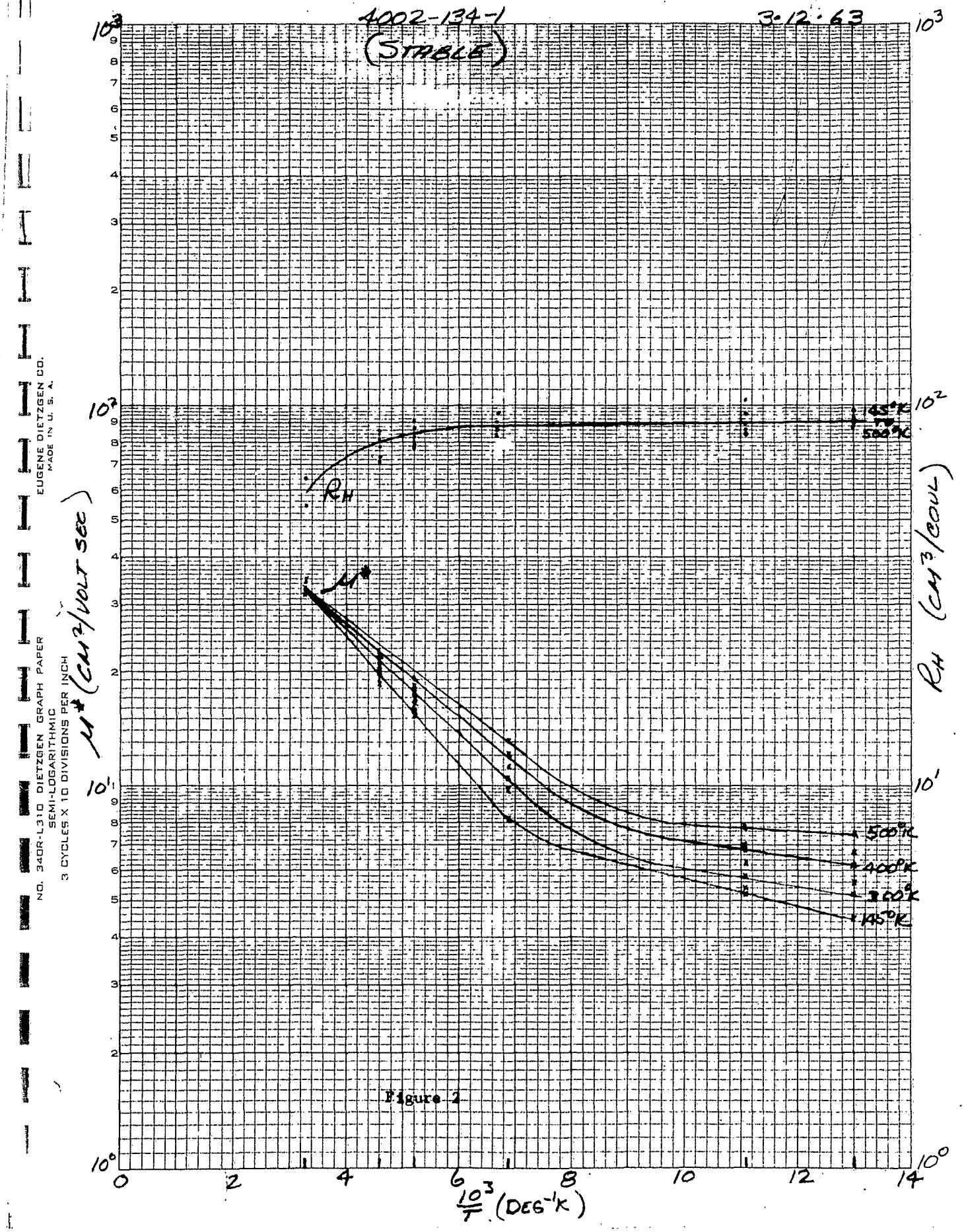

4002-134-1
(STABLE)
3·12·63
μ_H (cm²/volt sec)
R_H (cm³/coul)
$\frac{10^3}{T}$ (deg⁻¹K)
145°K
500°K
500°K
400°K
300°K
145°K
R_H
μ_H
NO. 340R-L310 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
3 CYCLES X 10 DIVISIONS PER INCH
EUGENE DIETZGEN CO.
MADE IN U. S. A.

Figure 2

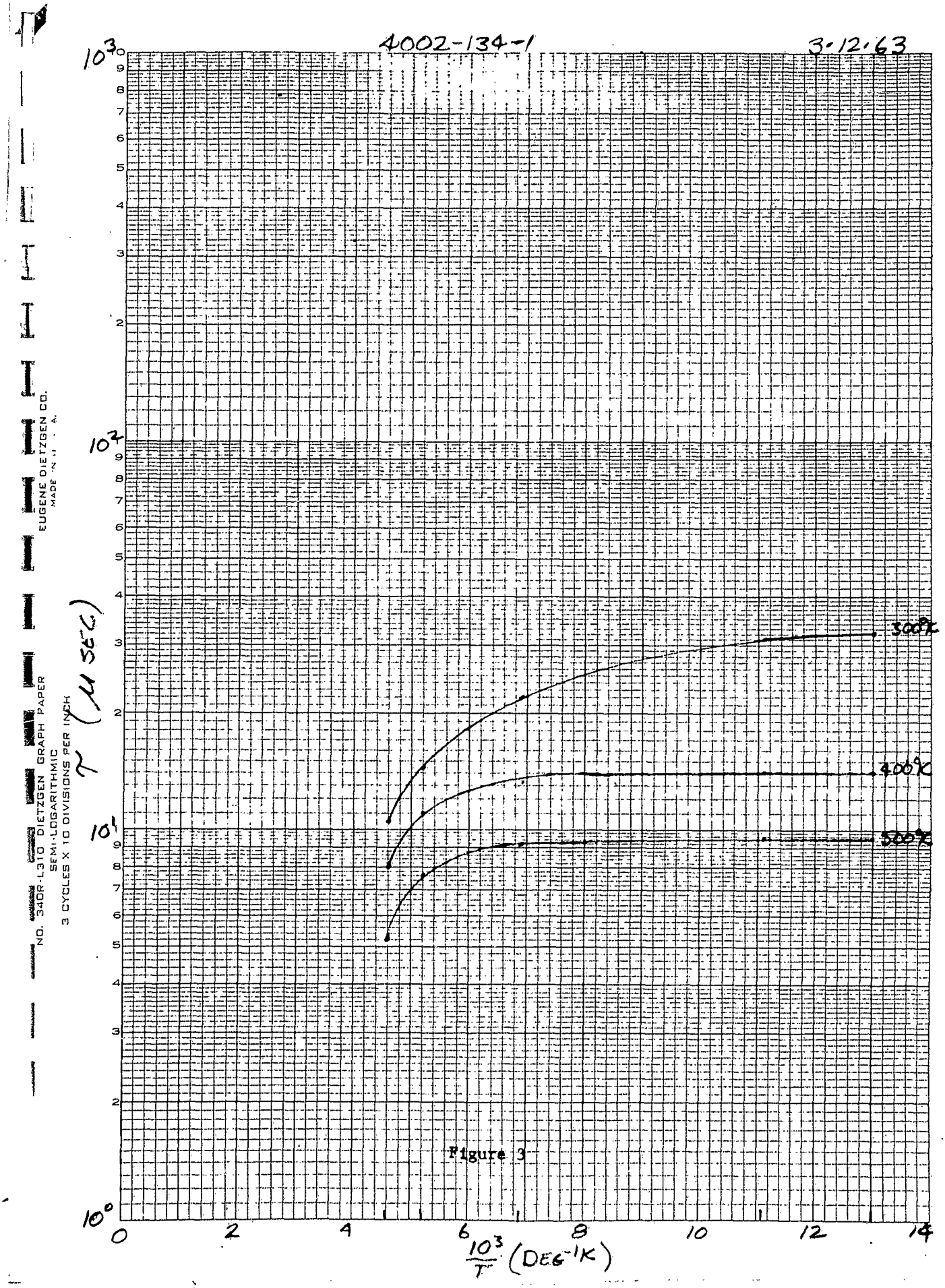

4002-134-1
3-12-63
10^3
10^2
10^1
10^0
T (μ sec)
300°K
400°K
500°K
0
2
4
6
8
10
12
14
$\frac{10^3}{T}$ (DEG^{-1}K)
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340R-L31D DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
3 CYCLES X 10 DIVISIONS PER INCH

Figure 3

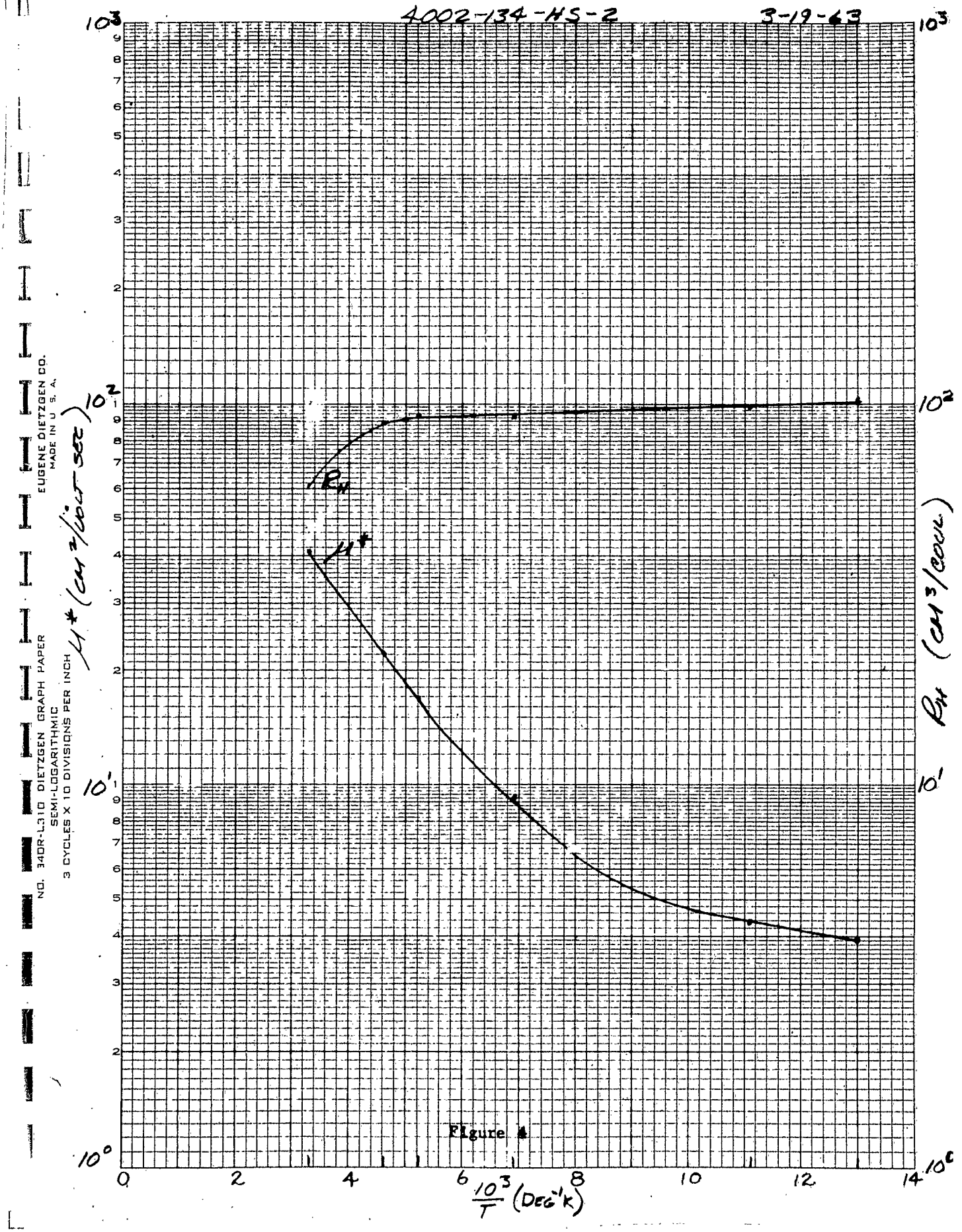

4002-134-HS-2
3-19-63
10^3
10^2
10^1
10^0
R_H
μ^*
μ^* (cm²/volt-sec)
R_H (cm³/coul.)
0
2
4
6
8
10
12
14
$\frac{10^3}{T}$ (Deg⁻¹K)
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340R-L310 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
3 CYCLES X 10 DIVISIONS PER INCH

Figure 4

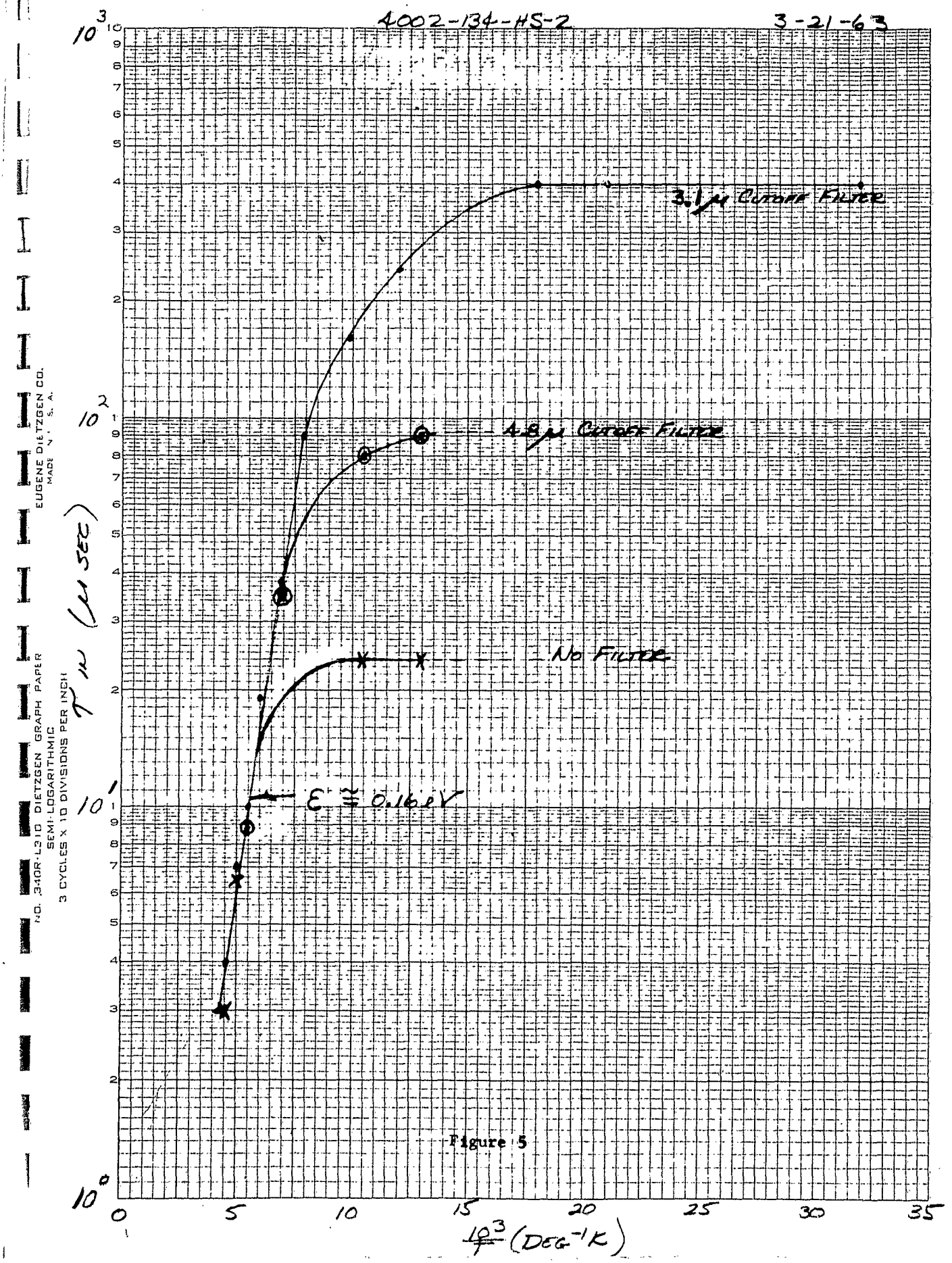
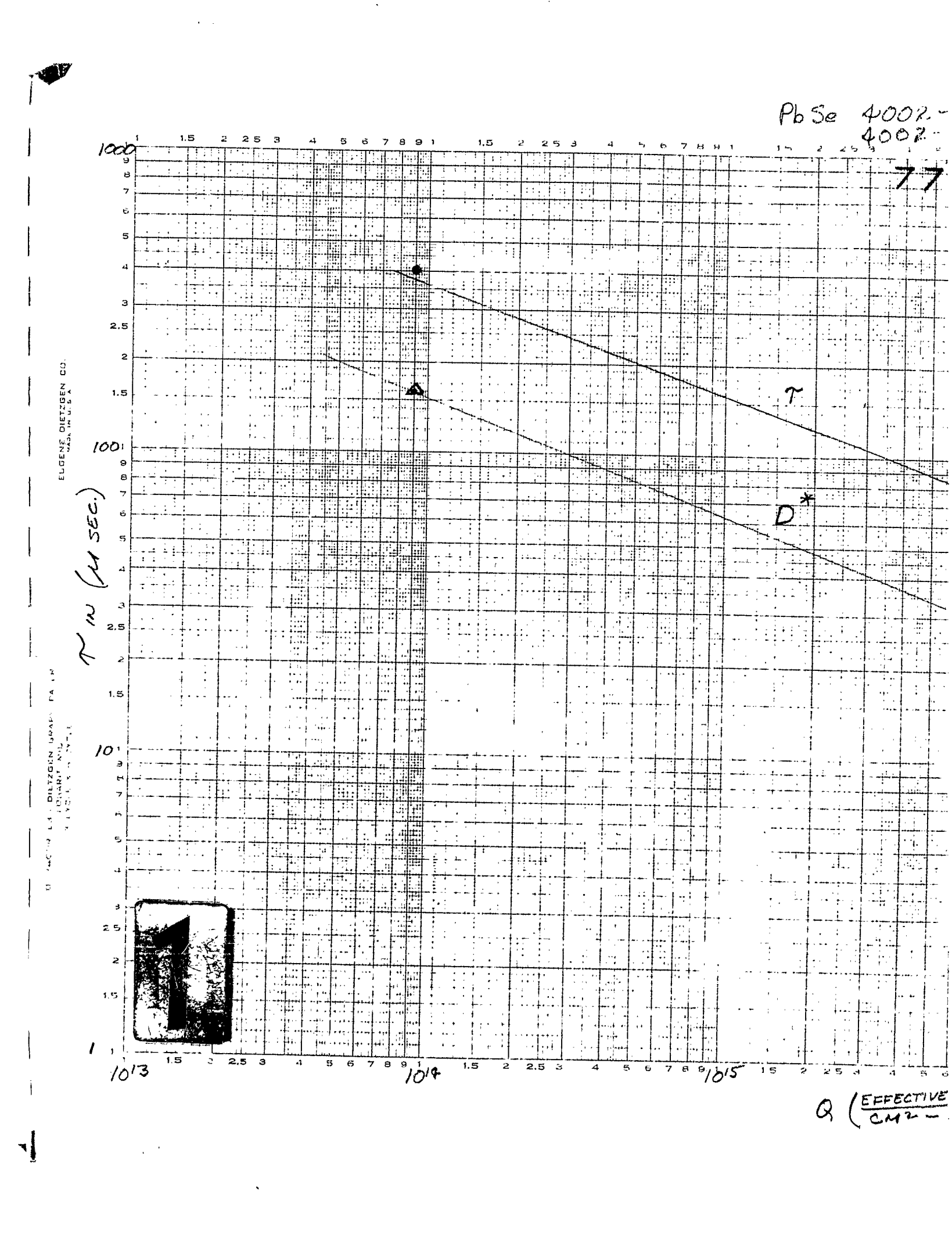

4002-134-HS-2
3-21-63
3.1 μ Cutoff Filter
4.8 μ Cutoff Filter
No Filter
ε ≅ 0.16 eV
τ in (μ sec)
10³/T (DEG⁻¹K)
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340R-L310 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
3 CYCLES X 10 DIVISIONS PER INCH

Figure 5

PbSe 4002.-
4002.-

77



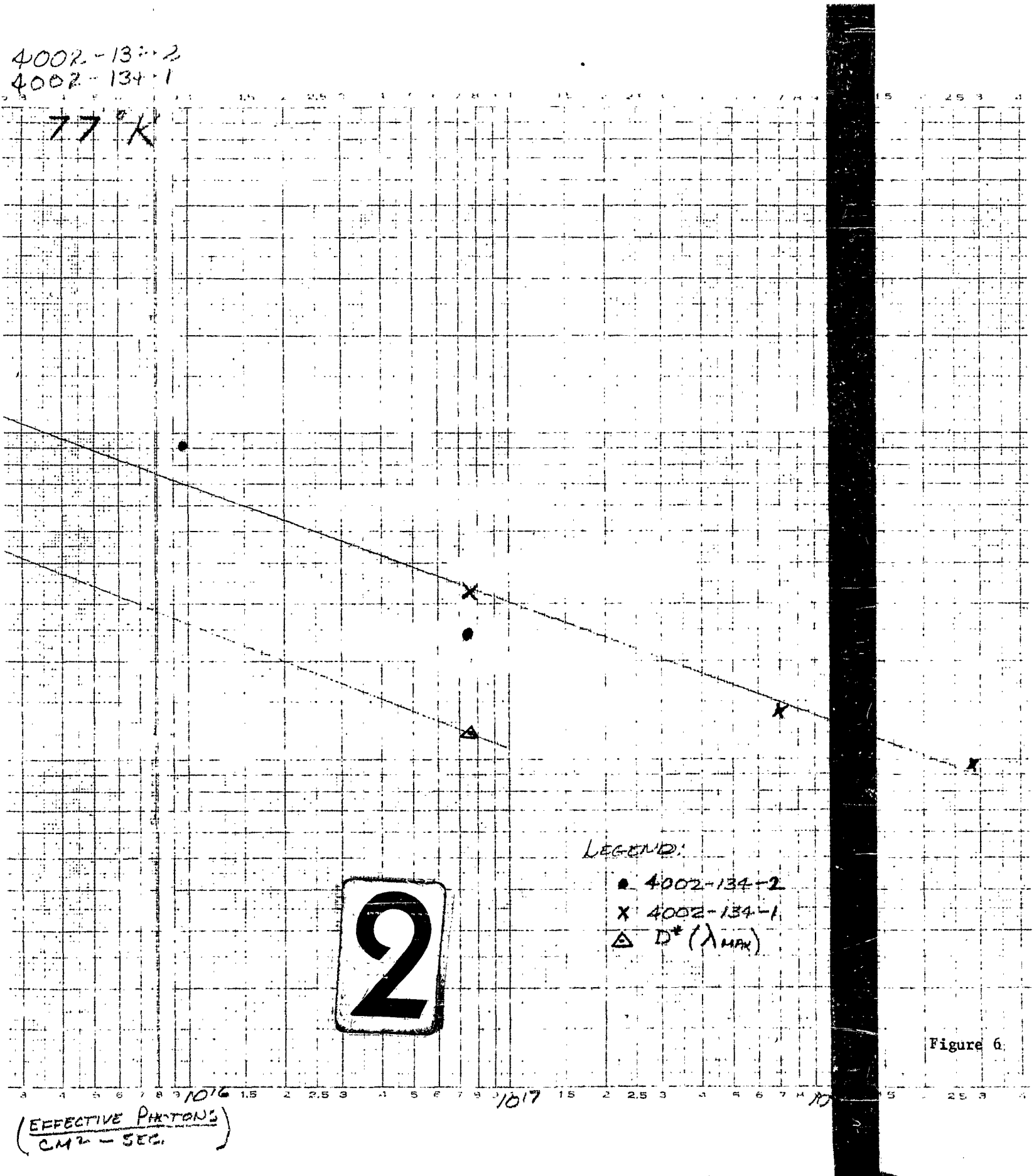

4002-134-2
4002-134-1
77°K
LEGEND:
● 4002-134-2
X 4002-134-1
△ D* (λMAX)
2
10^16
10^17
(EFFECTIVE PHOTONS / CM² - SEC.)

Figure 6.

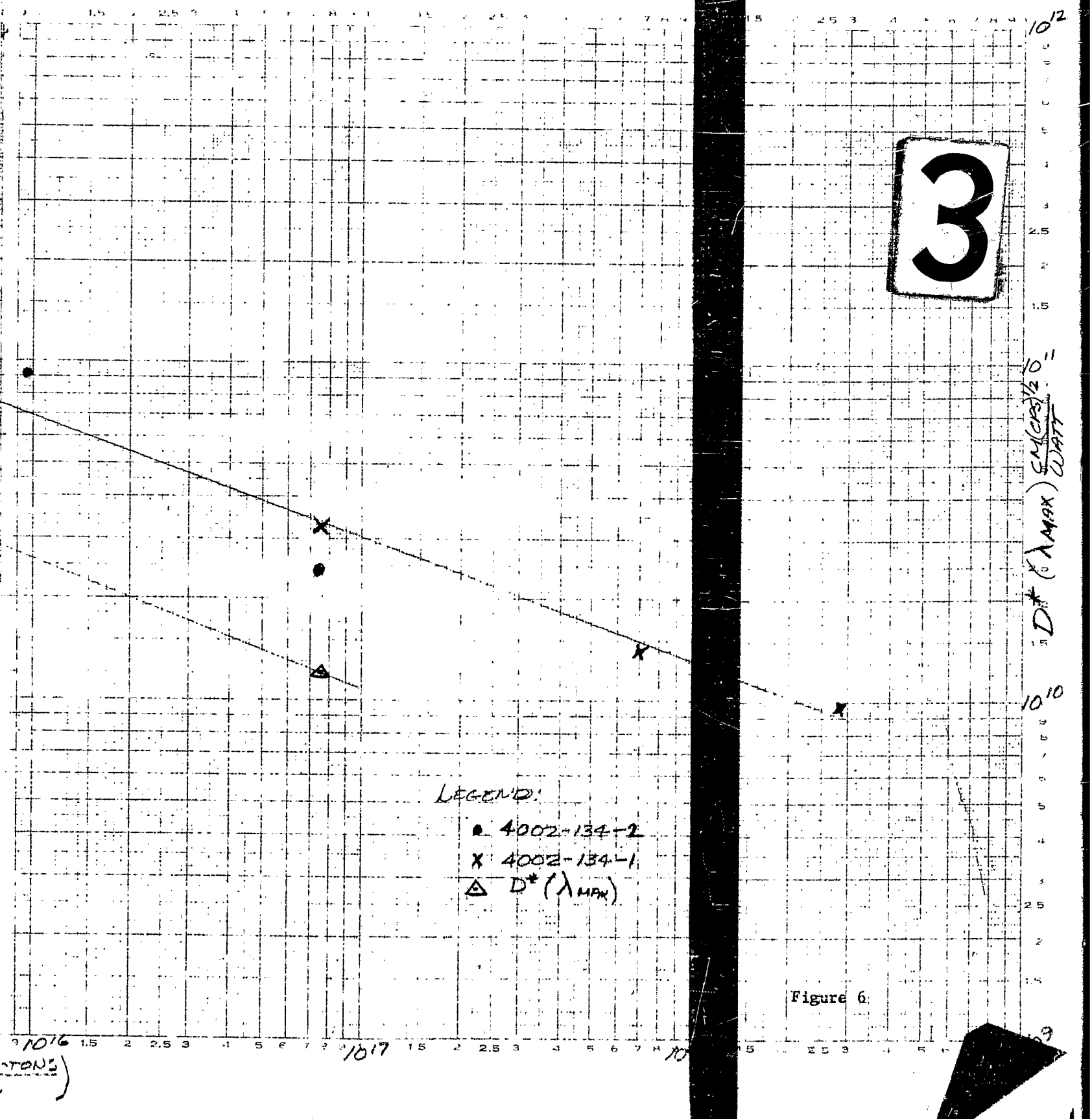
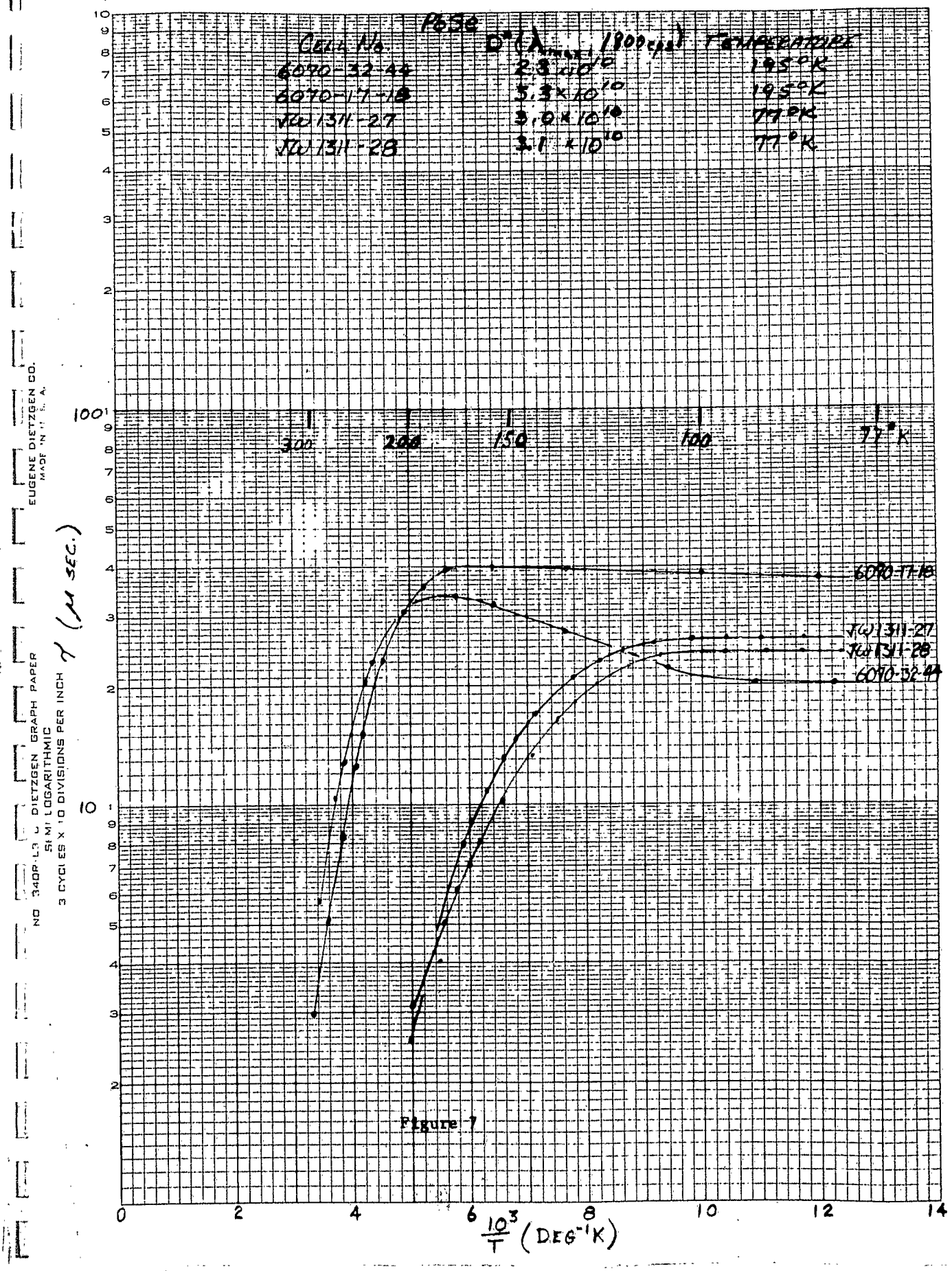

LEGEND:
● 4002-134-2
X 4002-134-1
△ D* (λ MAX)
D* (λ MAX) cm (cps)^1/2 / Watt
10^12
10^11
10^10
10^16
10^17

Figure 6


PbSe
Cell No.
6070-32-44
6070-1-7-18
TW1311-27
TW1311-28
D* (λmax, 1800 cps)
2.3 ×10^10
5.3 ×10^10
3.0 ×10^10
3.1 ×10^10
Temperature
195°K
195°K
77°K
77°K
300
200
150
100
77°K
6070-1-7-18
TW1311-27
TW1311-28
6070-32-44
τ (μ sec.)
10^3/T (DEG^-1 K)
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NO 340P-L3 DIETZGEN GRAPH PAPER
SEMI LOGARITHMIC
3 CYCLES X 10 DIVISIONS PER INCH

Figure 7